

## Occurrence and Fate of Organotins in a Waterworks in North China

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**Abstract** This paper first reports the occurrence and fate of monobutyltin, dibutyltin, tributyltin, monophenyltin, diphenyltin and triphenyltin in drinking water from north China. The sum of the six organotins in raw water and drinking water ranged from 33.3 to 476.9 ng Sn L<sup>-1</sup> and from no detection to 142.4 ng Sn L<sup>-1</sup>, respectively. The highest concentration of triphenyltin in drinking water and raw water were 41.3, 44.6 ng Sn L<sup>-1</sup>, and those for tributyltin were 32.1, 37.6 ng Sn L<sup>-1</sup>, respectively, which were observed from April to July. Conventional treatment processes and advanced treatment processes could not remove organotins completely.

**Keywords** Drinking water · Tributyltin · Triphenyltin · Advanced treatment

Organotin compounds, especially tributyltin (TBT) and triphenyltin (TPT) have been proven to be highly toxic to aqueous life and disturb the cell energy metabolism (Fent 1996) and the endocrine especially for dogwhelk (*Nucella lapillus*; Gibbs et al. 1991a). TBT and TPT pollution are

known to induce various symptoms on the affected organisms, like failure of spat in oysters (Alzieu et al. 1986), impotence in neogastropods and gastropods (Bryan et al. 1988; Gibbs et al. 1991b) and reduction of the dogwhelk population (Gibbs et al. 1991a). Organotins are also hazardous to humans, and butyltin and phenyltin compounds are both immunotoxic to human NK (natural killer) cells under in vitro experiments (Whalen et al. 2000). The estimated tolerable daily intake (TDI) value for TBTO and TPT acetate is 0.25 µg kg<sup>-1</sup> body weight as prescribed by the World Health Organization (WHO 1999) and 0.4 µg per kg body weight as prescribed by the German Federal Institute for Health Protection of Consumers and Veterinary Medicine (BGVV 2000), respectively.

Organotins are some of the most widely used organo-metallic compounds, and their world output has multiplied almost tenfold in the past 40 years, increasing from 5,000 tons in 1955 to approximately 50,000 tons in 1994 (Fent 1996). TBT is used worldwide as a biocide in antifouling paints on ships and in wood protection, and its global pollution has been well documented (Fent and Hunn 1995; Stab et al. 1996; Michel and Averty 1999). In contrast to TBT and its transformation products dibutyltin (DBT) and monobutyltin (MBT), data on the occurrence of TPT and its transformation products diphenyltin (DPT) and monophenyltin (MPT) in environment especially in fresh waters are relatively scarce (Fent and Hunn 1995; Gao et al. 2006). TPT has been used as co-toxicant with TBT in some antifouling paints, however, its major application lies in agriculture where it is used as a fungicide for various crops and released to aquatic ecosystems via leaching and runoff from agricultural fields.

To date, little is known about the occurrence, temporal variation and behavior of organotin compounds in drinking water. The investigations up to now are all related to DBT,

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MBT, dimethyltin (DMT) and monomethyltin (MMT), which are leaching from polyvinyl chloride (PVC) pipes (Braman and Tompkins 1979; Sadiki et al. 1996; Sadiki and Williams 1995, 1999). Residual levels of the above organotins in drinking water has created a new concern, and European countries have proposed banning the use of PVC for potable water transport (Richardson 2003). In this paper, the occurrence of butyltins (MBT, DBT, TBT) and phenyltins (MPT, DPT, TPT) in drinking water waterworks in north China is analyzed using solid phase microextraction (SPME)-GC-MS combined with ethylation by sodium tetraethylborate ( $\text{NaBEt}_4$ ). For removal of residual organotins from drinking water, the feasibility of an advanced treatment process including ozonization and activated carbon treatments processes were also investigated.

## Materials and Methods

Monobutyltin trichloride (MBT, 97%) and monophenyltin trichloride (MPT, 98%) were purchased from ACROS ORGANICS (Belgium). Dibutyltin dichloride (DBT, 97%), tributyltin chloride (TBT, 95%), triphenyltin chloride (TPT, 95%), tripropyltin chloride (TPrT, 95%) and sodium tetraethylborate ( $\text{NaBEt}_4$ , 98%) were purchased from Wako (Japan). Diphenyltin dichloride (DPT, 96%) was obtained from Aldrich, and tetrahydrofuran (HPLC grade) was from DIKMA (USA). Acetic acid and sodium acetate were purchased from a chemical plant in Beijing and were AR grade, hence were used without further purification. Water was obtained by a compact ultrapure water system (EASY pure UV, USA). Individual stock solutions of organotins ( $1,000 \text{ mg L}^{-1}$  as Sn) were prepared in methanol (HPLC grade). A working solution of mixed organotins containing  $200 \text{ mg L}^{-1}$  (as Sn) of each compound was also prepared using methanol as solvent. This solution was diluted in methanol as required. A 4% (w/v) solution of  $\text{NaBEt}_4$  was prepared with tetrahydrofuran every month. An acetate buffer (pH = 4) was made from acetic acid and sodium acetate solution. All the solutions were stored at  $4^\circ\text{C}$  in dark.

A SPME holder and a fiber coated with a  $100\text{-}\mu\text{m}$  layer of polydimethylsiloxane (PDMS) were obtained from Supelco (USA). A HP 5890 gas chromatograph equipped with a split/splitless injection port and coupled to a HP 5971 mass selective detector (Agilent Technologies Co., USA) using electron impact in the selected ion monitoring (SIM) mode were used. Separations were performed on a capillary column (HP-5MS,  $30 \text{ m} \times 0.32 \text{ mm i.d.} \times 0.25 \mu\text{m}$  coating thickness) throughout the experiment. The carrier gas was helium of high purity (99.9999%).

Water samples were manually collected in May, July, August, and September of 2003 and January, April, and

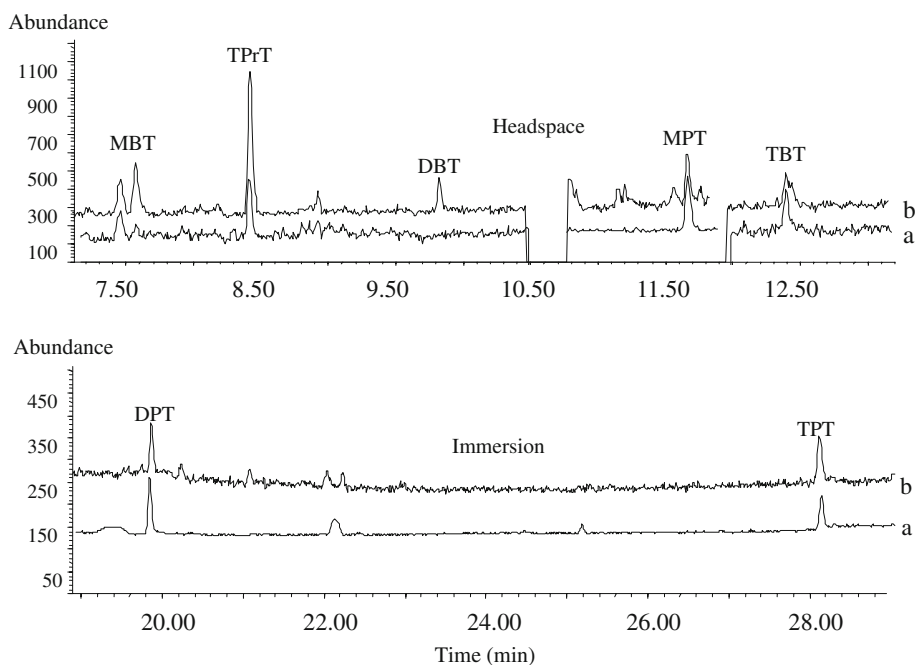
June of 2004 using amber glass bottles from a waterworks in north China. Raw water samples were collected from a reservoir for untreated water, while distribution water samples were directly collected from a tap of the residential area. Distribution pipes are all galvanized iron pipes in this waterworks. The unacidified and unfiltered samples were stored at  $4^\circ\text{C}$ .

Appropriate amounts of TPrT internal standard were added into 22 (or 28) mL of water samples in 40-mL amber glass vials sealed with PTFE-lined silicon septa. After adding 2 mL acetate buffer and 0.1 mL 4%  $\text{NaBEt}_4$  solution, the vials were immediately closed and the contents were stirred on a magnetic stirrer. Then the SPME fiber was exposed to the headspace over the vigorously stirred solution at room temperature to analyze TBT, DBT, MBT and MPT; or immersed into the solution to analyze TPT and DPT. After 20 (or 60) min, the fiber was withdrawn and inserted into the needle of the holder, and the SPME was placed in the GC injector. The temperature programs used for the GC column were:  $60^\circ\text{C}$  for 2 min,  $20\text{--}130^\circ\text{C min}^{-1}$ ,  $5\text{--}250^\circ\text{C min}^{-1}$ , then  $20\text{--}280^\circ\text{C min}^{-1}$ , hold 1 min. The temperatures of the injector and detector were 270 and  $280^\circ\text{C}$  respectively. An internal standard quantification strategy was employed to minimize the response variation. The precision was estimated by analyzing five samples containing  $20 \text{ ng Sn L}^{-1}$  for each compound, and the RSD was less than 8%. The limits of detection (LODs) for MBT, DBT, TBT, MPT, DPT and TPT in selected ion monitoring (SIM) mode (S/N = 3) were 0.95, 1.23, 1.67, 2.16, 2.21,  $2.28 \text{ ng Sn L}^{-1}$ , respectively, and no blank values were found for them.

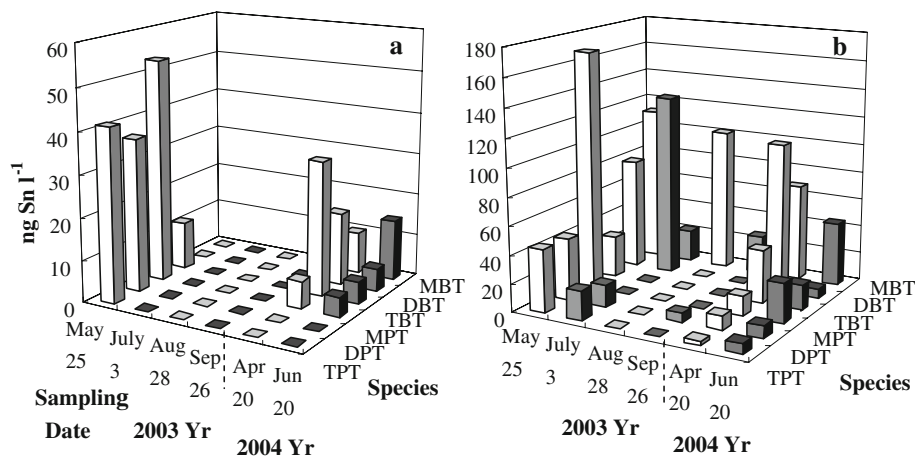
## Results and Discussion

Figure 1a shows the chromatograms of organotins in the tap water taken on May 25, 2003 from a waterworks in north China for evaluating the occurrence of organotins in drinking water. While TBT ( $11.4 \text{ ng Sn L}^{-1}$ ), MPT ( $53.2 \text{ ng Sn L}^{-1}$ ), DPT ( $36.5 \text{ ng Sn L}^{-1}$ ) and TPT ( $41.3 \text{ ng Sn L}^{-1}$ ) were simultaneously detected in this sample, no MBT and DBT were found. Figure 2a shows the occurrence of organotins in drinking water in May, Jul, Aug, Sep 2003 and in Apr, Jun 2004. It was found that organotins (TBT, MPT, DPT and TPT) in tap water were detected on May 25, 2003, and MBT, DBT, TBT and MPT were detected on April 20 and on June 20, 2004 simultaneously, but no organotins were found (below the detection limits) in July 3, August 28, or September 26, 2003. Although several previous papers have reported the occurrence of MMT, DMT, MBT, and DBT in drinking water in Florida (USA) and Canada (Braman and Tompkins 1979; Sadiki et al. 1996; Sadiki and Williams 1995,

**Fig. 1** Chromatograms of organotins in water samples taken on May 25, 2003. **a** tap water; **b** raw water. Extraction ion: 149 for MBT, DBT, TPrT and TBT; 197 for MPT, DPT and TPT



**Fig. 2** Occurrence of organotins in drinking (a) and raw (b) water from a water supply system between 2003 and 2004



1999), the occurrence of TBT and phenyltins in drinking water was first reported in this paper. At present, there is still no drinking water criterion set of organotins in China and other countries. It should be noted that the concentrations of TBT in drinking water in May 25, 2003, April 20 and June 20, 2004 reached 11.4, 32.1, and 5.1 ng Sn L<sup>-1</sup>, respectively, which were all higher than the criterion (1 ng L<sup>-1</sup>) for protecting saltwater aquatic life from chronic toxic effects (US EPA-822-B-02-001 2002).

Since some of the organotin compounds were found in drinking water from the waterworks in north China, the occurrence of organotins in corresponding raw water was also investigated. In contrast to drinking water, we added a raw water sample collected in January 25, 2004. Figure 1b shows the chromatogram of organotins in the raw water sample taken on May 25, 2003. The analytical results

indicated that the six organotins including MBT, DBT, TBT, MPT, DPT and TPT were also detected simultaneously, and their concentrations were 111.4, 78.8, 29.4, 168.7, 44.0, and 44.6 ng Sn L<sup>-1</sup>, respectively. Figure 2b shows the temporal variation in the level of organotins in the raw water. The concentrations of all the organotin compounds varied greatly with passing time, and the sum of the compounds in raw water ranged from 33.3 to 476.9 ng Sn L<sup>-1</sup>. Of the six organotins, only MBT was detected in all seven samples, and random variations in the concentration were found. The highest concentrations for MBT, DBT, TBT, MPT, DPT and TPT were found to be 111.4, 129.5, 37.6, 168.7, 44.0, and 44.6 ng Sn L<sup>-1</sup>, respectively. Because the distribution pipes used in this waterworks are all galvanized iron pipes, the organotins in drinking water can mainly consider to be originated from

**Table 1** Changes in organotins levels (ng Sn L<sup>-1</sup>) in the conventional treatment process and advanced treatment process for drinking water

Sampling time			Organotins					
			MBT	DBT	TBT	MPT	DPT	TPT
Conventional treatment process (2003 year)	May 25	Raw water	111.4	78.8	29.4	168.7	44.0	44.6
		Tap water	ND <sup>a</sup>	ND	11.4	53.2	36.5	41.3
	Jul 3	Raw water	22.4	129.5	ND	ND	15.7	20.9
		Tap water	ND	ND	ND	ND	ND	ND
	Aug 28	Raw water	101.3	ND	ND	ND	ND	ND
		Tap water	ND	ND	ND	ND	ND	ND
	Sep 26	Raw water	26.8	ND	ND	ND	6.5	ND
		Tap water	ND	ND	ND	ND	ND	ND
Advanced treatment process (2004 year)	Apr 20	Raw water	68.5	104.9	37.6	14.0	10.2	2.9
		Tap water	9.9	17.3	32.1	6.5	ND	ND
	Jun 20	Raw water	44.9	6.6	17.9	27.9	8.7	7.0
		Tap water	14.5	5.4	5.1	4.6	ND	ND

<sup>a</sup> ND indicates that the concentration was below the LOD

raw water. This result is different from that reported in previous papers, in which the occurrence of organotins in drinking water was mainly attributed to the leaching of the distribution system (Sadiki et al. 1996; Becker et al. 1997; Sadiki and Williams 1999), as the pipes were made of PVC.

Generally, TBT and TPT in the aquatic environments are mainly due to leaching from anti-fouling paints and agricultural application of pesticides, although these chemicals are also used as preservative for timber. And it was reported that TBT was often detected in the summer due to boat activity (Morabito 1995), but in this paper, the TBT was detected in spring. Thus, the identification of its potential pollution source occurring in raw water is necessary. On the other hand, high concentrations of butyl- and phenyltin occurred during the spring (in April and May) when agricultural pesticides were largely used, suggesting that the pollution of organotins in raw water would originate from agricultural application. This result is similar to the report of Bancon-Montigny et al. (2004).

The conventional treatment processes of the waterworks included flocculation, filtration, and NaOCl disinfection, and the advanced treatment processes consisted of pre-oxidation, flotation, filtration, ozonization, activated carbon and NH<sub>2</sub>Cl disinfection. In the conventional treatment process, the dosages of NaOCl were ranged from 3.46 to 5.42 mg/L, and the dosages of FeCl<sub>3</sub> for flocculation were from 1.89 to 22.9 mg/L. In the advanced treatment processes, KMnO<sub>4</sub> (0.3–1.05 mg/L) was used for preoxidation; 6–8.79 mg/L FeCl<sub>3</sub> was added before flotation with regurgitant ratio of 9.6%–12%; and the dosage of ozone was 1.75–4.57 mg/L. The organotin levels in conventional treatment processes in May, Jul,

Aug, Sep 2003 and advanced treatment processes (a pilot plant) in Apr and Jun 2004 were shown in Table 1. From Table 1, it was found that six organotin compounds were all detected in raw water taken in April and June 2004, and the total organotin concentrations were 238.1 and 113.0 ng Sn L<sup>-1</sup>, respectively. After advanced treatment processes, DPT and TPT were not detected in drinking water, while the removals for DPT and TPT in traditional treatment processes in May 25, 2003 were only 17% and 7%. The organotin compounds except for DPT and TPT were still residual in drinking water, and the removals of MBT, DBT were respectively 77% and 51%, which were lower than those in conventional treatment processes. In addition, 43% TBT and 69% MPT were removed from raw water which was similar with those in conventional treatment processes. And further research is necessary before inferring about the efficacy of both conventional and advanced treatment processes in removing these compounds. In a word, both conventional and advanced treatment processes described in this paper can remove some organotins, but cannot remove six organotins completely, suggesting that a more suitable and efficient treatment process should be considered.

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